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THE PERMEABILITY OF PLASTIC FILMS AND FOILS TO GASES, VAPORS AND LIQUIDS

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P.T.van Raaij and P.Winkel

ABSTRACT. The basic theories of the permeability of thin macromolecular films to small molecules are reviewed, with mathematical formulas and graphs on irradiated and non-irradiated polyethylene and cellophane permeability. Factors affecting permeation, such as temperature and pressure, chemical nature and geometry of diffusing substances and chemical nature and molecular structure of the polymer films are discussed. Laminates of paper/plastic and metal/plastic for special purposes, including protection from poison gases, are described briefly.

NOTATIONS

/2

$C\left[\frac{gm}{cm^3}\right]$ = concentration penetrant in polymer

$D\left[\frac{cm^2}{sec}\right]$ = diffusion constant

$D_o\left[\frac{cm^2}{sec}\right]$ = diffusion constant for $T = \infty$

$E_d\left[\frac{cal}{mol}\right]$ = activation energy for diffusion

$E_p\left[\frac{cal}{mol}\right]$ = activation energy for penetration

$\Delta H\left[\frac{cal}{mol}\right]$ = heat of solution penetrant in polymer

$J\left[\frac{gm}{cm^2 sec}\right]$ = diffusion current density

l[cm] = thickness of film

p[cm Hg] = gas pressure penetrant

$P\left[\frac{gm}{cm\ sec\ cm\ Hg}\right]$ = permeability coefficient

$P_o\left[\frac{gm}{cm\ sec\ cm\ Hg}\right]$ = permeability coefficient for $T = \infty$

$Q\left[\frac{gm}{cm^2}\right]$ = mass rate of flow through film

$R\left[\frac{erg}{mol\ ^oK}\right]$ = universal gas constant

$S\left[\frac{gm}{cm^3\ cm\ Hg}\right]$ = solubility coefficient

$S_o\left[\frac{gm}{cm^3\ cm\ Hg}\right]$ = solubility coefficient for $T = \infty$

$T[^oK]$ = absolute temperature

t[sec] = time

* Numbers in the margin indicate pagination in the foreign text.

1. Introduction

The fact that plastics today are virtually indispensable in many fields needs no further elaboration.

A very important application of such plastics is in the field where use is made of the specific permeability of plastic foils and films to gases, vapors, and liquids. In general, one could think in this respect of the packaging industry in particular of so-called impermeable protective wrapping, and of the paint industry where, in this particular case, material surfaces are provided with plastic coatings "impermeable" to poison gas. For such purposes, usually foils or films of maximum density are required. In special cases, selective permeability might be required, among others for the separation of gases or azeotropic mixtures of liquids and other systems that are difficult to separate, e.g., isomers or isotopes.

The theory of permeability (or the permeation process) to gases has been described in detail in the literature (Ref.1, 2, 3). Furthermore, numerous methods have been described for determining the rate of penetration of gases such as air and water vapor (Ref.4, 5, 6, 7, 8). Little, however, has been published to date on liquid penetration, either as to its theory or as to experiment (Ref.9, 10, 11). Plastics in general, and plastic films in particular, may play an important role in the overall concept of protective measures in chemical warfare. Therefore, for a number of years, close attention has been paid at the Chemical Laboratories RVO-TNO to such application possibilities. The results /2 obtained in these investigations will be presented in future reports. It seems useful to present here the principal theoretical background of the investigations as an introduction.

2. General Aspects of the Permeation Process

It has been established, from numerous investigations on the permeability of films to gases, that the penetration through plastic foils does not take place via macro- or micropores and that plastic films of customary thickness (generally greater than 0.025 mm) must be considered to be free of pores (Ref.1).

That penetration nevertheless takes place is due to the thermal action of the polymer chain members, whereby holes of molecular dimensions are formed.

These holes are variable as to time and location and thus cannot be considered as actual pores.

The permeation process therefore must be interpreted as a diffusion of the dissolved molecules of the penetrating compound (penetrant) through temporarily opened holes of molecular size (so-called "kinetic" porosity, an extreme example of which is given by the liquid model). This is an activated diffusion whose velocity greatly increases with temperature. An exponential function has been found for the dependence on temperature, analogous to the Arrhenius equation which is valid for processes requiring an activation energy.

The term "solution diffusion" is sometimes used. The diffusing molecule is

thought to be dissolved in a hole in the polymer until another hole is opened nearby to which it can migrate. By such repeated displacements, the molecule advances (stepwise) through the polymer in the direction of decreasing concentration, until it finally escapes on the low-pressure side.

The diffusion of the separate molecules of the dissolved gas in the polymer proceeds therefore by (statistic) exchange of places. /3

The velocity of the process is characterized by the diffusion coefficient which is a measure of the probability that a penetrant molecule will be displaced in unit time from its position of equilibrium within the polymer to a new position of equilibrium, a short distance in the direction of the diffusion current.

The required energy for this process is produced by the activation energy necessary to form a hole in the new position of equilibrium, just preceding the displacement of the penetrant molecule in question.

The energy and entropy of activation in this process are predominantly connected with the random thermal agitation of the polymer chain members.

Summarizing, the permeation process or, in other words, the behavior of the penetrating substance, can be described as follows:

1) solution at the film surface in the material;
2) diffusion through the film, under the influence of a concentration gradient (diffusion as in a liquid);
3) evaporation at the other side of the film (desorption from the "solution").

2.1 Permeation of Gases

Some laws on permeation can be derived from the model in Fig.1.

If the boundary surfaces of the film are kept at constant concentration, at $x = 0 \rightarrow c = c_1$ (for each time) and at $x = l \rightarrow c = c_2$ (for each t) where $c_1 > c_2$, respectively, a steady state sets in after a relatively short starting period. This means that the concentration remains constant at all points of the film, /4 so that the following is valid for one-dimensional diffusion:

$$\frac{\delta c}{\delta t} = 0. \qquad (1)$$

From this, it follows that

$$\frac{\delta^2 c}{\delta x^2} = 0 \text{ [App. I eq.(3)]}.$$

Integration with respect to x yields $\frac{\delta c}{\delta x} = \text{const}$ from which we obtain after

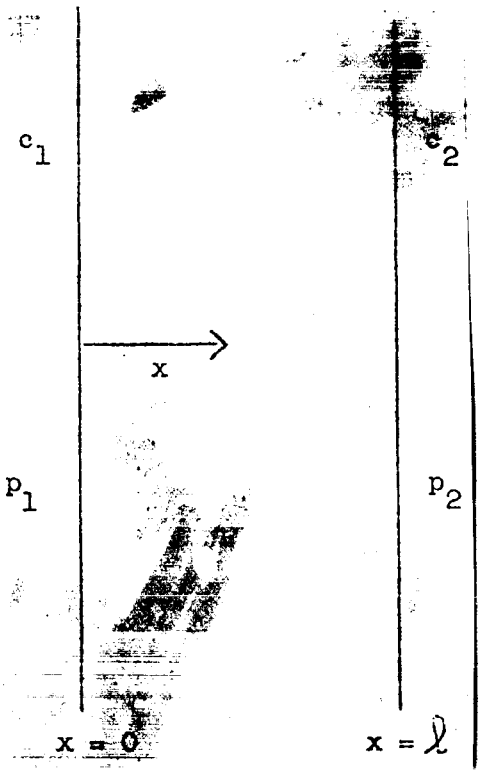

Fig.1

further integration and introduction of the conditions for

$$x = 0, \text{ and } x = \ell \longrightarrow \frac{c - c_1}{c_2 - c_1} = \frac{x}{\ell} .$$

This yields a concentration course as /5 indicated in Fig.2.

Thus, the concentration c of the penetrant in the film varies linearly with x.

The diffusion current density J gives the amount of gas diffusing in unit time and unit area, represented by $J = -D \frac{dc}{dx}$ [App.I, eq.(2)].

Therefore, for $\frac{dc}{dx}$ = const, J also is a constant.

Integrated, this yields

$$J = D \frac{(c_1 - c_2)}{\ell} . \qquad (4)$$

Often the surface concentrations c_1 and c_2 are not known, but only the gas or vapor pressures p_1 and p_2 on either side of the membrane.

For the solubility of gases in macromolecular substances, the law of distribution applies to the concentration in both phases:

$$\frac{c_{\text{phase 1}}}{c_{\text{phase 2}}} = K\,(T) \quad (T = \text{absolute temperature}).$$

In the vapor phase (phase 2), under assumption of the equation of state for /6 ideal gases, the concentration can be replaced by the pressure p. Then, in accordance with the Henry-Dalton law, we obtain the following for the concentration of the gas in the film surface:

$$c = \frac{K(T)}{RT} p.$$

When using the symbol S(T) for $\frac{K(T)}{RT}$, we thus obtain

$$c = S(T)p . \tag{5}$$

Here, R is the gas constant and S the solubility coefficient. Combination of eqs.(4) and (5) now yields

$$J = \frac{DS(p_1-p_2)}{\ell} = \frac{P(p_1-p_2)}{\ell} . \tag{6}$$

A new quantity P = DS has been introduced here, called the permeability constant. P (and also D and S) is dependent only on the concentration or pressure difference and not on the concentrations or pressures themselves.

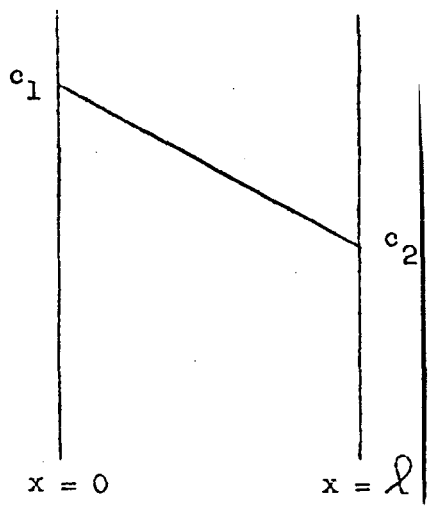

Fig.2

For gases such as H_2, N_2, O_2, CO_2, and H_2S, at moderate pressures (up to about 7 atm), no influence of the pressure on P was noted in numerous plastic foils (Ref.1, 5). An influence of pressure was observed only for vapors which dissolve in the foil in large quantity.

This is due to the fact that, for readily condensable gases (vapors), the law of distribution is valid only at low concentrations or pressures.

At higher pressures, considerable deviations occur. Furthermore, the diffusion coefficient /7 in this case is often variable with the concentration. The value of D, derived from measurements at steady flow, here represents a mean value for the concentration range in question.

Equation (4) must now be substituted by

$$J = \frac{\bar{D}(c_1-c_2)}{\ell} \tag{7}$$

where

$$\bar{D} = \frac{1}{c_1-c_2} \int_{c_2}^{c_1} D\,dc . \tag{8}$$

Thus, $\bar{D}$ is the mean value, derived from measuring the diffusion current density in the steady state. In the case of concentration-dependent D, the concentration is naturally no longer linearly dependent on the distance x in the membrane in steady flow.

For the above reason, stipulation of a single permeability coefficient $J = P \frac{p_1 - p_2}{l}$, calculated from eq.(6), is frequently insufficient to characterize the permeability.

It is true that P always has been found to be independent of the thickness l of the membrane.

The above-described steady state does not set in immediately but is preceded by a certain start-up time, as indicated in Fig.3.

At a given time t_d, the permeation manifests itself via the detection method used.

The time t_d, which can be denoted as permeation time, thus varies with the sensitivity of the detection method. The point t_e, which is found by extending the straight line of the steady state to the time axis, can be determined much more accurately. Since, at the instant of time t_e, a certain amount of substance has already permeated, this time is generally not applicable as determining quantity in the case of poison gases. In that case, one must rely on a determination of the permeation time whose standardization has remained a difficult matter in connection with variations in sensitivity of the detection method. /8

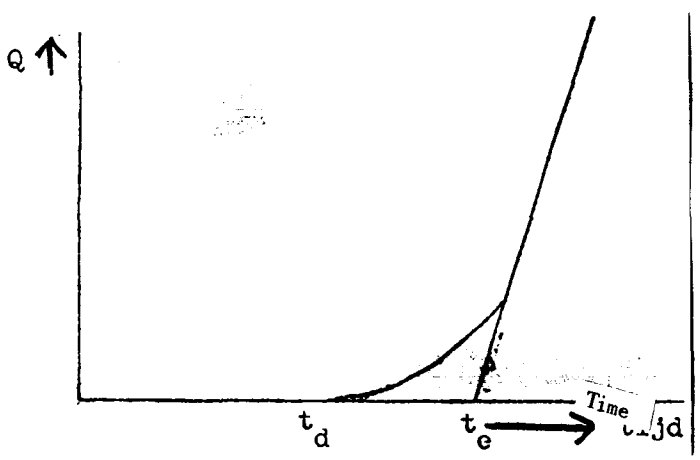

Fig.3 Permeated Amount Q as a Function of Time.

2.2 Liquid Permeation Process

The general mechanism of the liquid permeation process is analogous to that of gas permeation.

There are, however, important differences in the state of the permeable membrane and in the rate of transfer of substance through the membrane.

During the permeation of gas, the properties of the polymer film are not changed appreciably by the permeating gas, since the latter has a very low degree of solubility in the film (so-called "dry" film).

Thus, it is here possible to calculate the composition of the permeate of a mixture from the permeation rate of pure gases and their composition.

In the permeation of organic vapors or of liquids, it is not possible to calculate the composition of the permeate from the composition of the mixture and /9

from the permeation rate of the pure components.

The swollen membrane, i.e., the membrane containing the dissolved permeating components (a "solution" of polymer and permeating organic compounds), has an essentially different permeability than the original membrane. Similarly, on penetration of individual substances, the state of the membrane differs from that on penetration of a mixture of heterogeneous molecules.

Fick's First Law is valid for the description of liquid permeation in the steady state:

$$J = \frac{\bar{D}(c_1 - c_2)}{l} \qquad \text{[see eq. (4)]}$$

where J again is the diffusion current density; $\bar{D}$ is the mean diffusion coefficient according to eq.(8).

In selecting foils for protection from poison gases, generally a polymer is used which exhibits little interaction with such gases, resulting in a low solubility. For this application, the dependence of D on the concentration will probably not be excessive. Within the range of 1 - 8 atm, the penetration is not influenced by pressure on the liquid (Ref.10). This is so, since the solubility in the polymer is independent of the pressure, so that the concentration gradient remains unchanged.

The pressure at the permeate side of the film has very little influence on the permeation rate as long as the permeate is rapidly dissipated in the form of vapor. The permeation rate is then independent of the pressure difference over the film.

Simple calculations show that the molecular concentration in the liquid /10
phase of the permeate is so large with respect to the concentration in the vapor phase, that the concentration gradient is hardly influenced by changes in permeate pressure (e.g. from 20 to 500 mm Hg) . Often the liquid permeation actually takes place more rapidly than the permeation from the saturated vapor phase. From the thermodynamic viewpoint, this would not be expected since the chemical potential μ of a substance, in two phases in equilibrium with each other, is the same. Thus, the concentration of a penetrating substance in the surface layer of the film should be the same for liquid and saturated vapor. Since the velocity-determining process in permeation normally is the diffusion through the film due to the concentration gradient, the same rate of permeation would be expected for steady flow.

Nevertheless, the permeation velocity, upon liquid contact with the film, may be many times greater than upon contact of saturated vapor with the film.

The lower permeation rate for the saturated vapor phase apparently must be ascribed to the lower rate of transfer of matter to the film surface. Fresh vapors apparently cannot be supplied rapidly enough to maintain a continuous high concentration of the rapidly permeating and highly soluble penetrant in the film

surface. It is also possible that, upon contact with liquid, the film surface is in a more swollen and "open" condition that upon contact with saturated vapor.

3. Factors Influencing the Permeability of Plastic Films

3.1 Temperature

For the diffusion coefficient D as well as for the solubility coefficient S there exists an exponential dependence on the temperature, analogous to the Arrhenius equation

/11

$$S = S_o e^{-\frac{\Delta H}{RT}} \tag{9}$$

where S_o is the solubility coefficient for $T = \infty$; ΔH is the heat of solution; R is the universal gas constant; T is the absolute temperature.

Also,

$$D = D_o e^{-\frac{E_d}{RT}} \tag{10}$$

where D_o is the diffusion coefficient for $T = \infty$ and E_d is the activation energy for diffusion.

Furthermore,

$$P = DS = D_o S_o e^{-\frac{1}{RT}(\Delta H + E_d)} = P_o e^{-\frac{E_p}{RT}}. \tag{11}$$

The penetration, therefore, is an activated process. $P_o = D_o S_o$ is the permeation coefficient for $T = \infty$; E_p is the activation energy for permeation:

$$E_p = \Delta H + E_d. \tag{12}$$

Thus, a linear relationship exists between log P and $\frac{1}{T}$ (with T being the absolute temperature), which has been determined in detail by experiment (see Fig.4); (Ref.1, 4, 5).

/12

The activation energy can be calculated from the slope of the straight line.

The diffusion constant always increases with increasing temperature, meaning that the activation energy of diffusion E_d is positive.

For permanent gases, the heat of solution ΔH is small but positive (heat is required for the dissolving); therefore, the solubility increases slightly with the temperature.

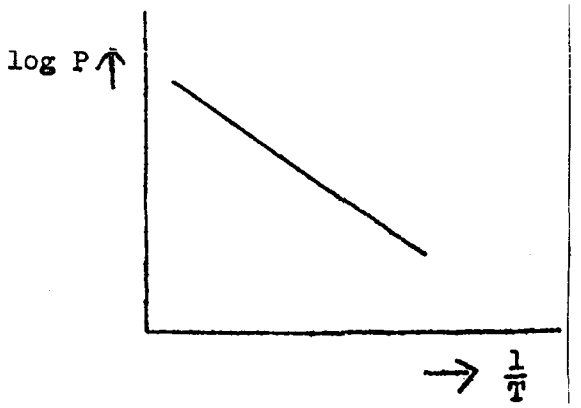

Fig.4 Correlation between permeability Coefficient and Absolute Temperature.

Consequently, the permeability to permanent gases always increases with increasing temperature.

For readily condensable vapors, ΔH is negative (because of the influence of the heat of condensation), so that the solubility decreases with rising temperature. At high solubility of the vapor ($\Delta H < 0$) and low activation energy for diffusion, the activation energy may become zero or negative; the permeation is then independent of the temperature or decreases with increasing temperature. However, it has been determined experimentally that the permeability almost always increases with rising temperature (Ref.1, 4, 5). In the case of liquid, the contribution of the heat of condensation is lacking. Consequently, the permeation rate will increase with increasing temperature.

However, at strong interaction between liquid and polymer, the heat of solution may even be negative so that the solubility will decrease with increasing temperature.

In this case, the rate of penetration will increase with decreasing temperature. This, however, will occur only at strong interaction between liquid and polymer, a situation to be avoided as much as possible in the case of protective materials from poison gases.

As soon as a first-order or second-order transition point is reached, a distinct change takes place in the permeability, diffusion constant, and solubility coefficient over a narrow temperature range, as a result of the change in the mobility of the chain members of the polymer molecule. /13

3.2 Pressure

It was noted already that the permeability constants for "permanent" gases (O_2, N_2, CO_2, etc.) are independent of pressure.

In the case of organic vapors, the permeability constant is dependent on the pressure and generally increases with rising pressure.

This effect can be ascribed to an increase in the diffusion constant because of the plasticizing effect of the absorbed vapor and to an increase in the solubility coefficient (as a result of the slope of the sorption isotherm). The

permeability constant of water vapor is independent of the pressure or increases with increasing pressure, depending on the nature of the film (hydrophobic or hydrophilic).

The behavior of water, however, can be anomalous and may be complicated since solubility and diffusion are strongly pressure-dependent, especially at high relative humidity.

The "non-ideal" solubility behavior can be partially explained by assuming a bunching of the strongly polar water molecules in the case of hydrophobic films such as rubber and polyethylene (clouding of the foil, lowering of the diffusion coefficient due to bunching at rising concentration). Another explanation is the high degree of polymer-water interaction in the case of hydrophilic films such as cellophane or polyvinyl alcohol. /14

It was noted already that, for gases and vapors, the rate of permeation is proportional to the pressure difference over the film.

3.3 Nature, Shape, and Dimensions of the Diffusing Molecules

Since the permeation is connected with the solubility and diffusion rate, the influence of the above factors on the permeation must be investigated.

The nature of a diffusing molecule is expressed by its interaction.

If the interaction forces between the molecules of a given substance are strong, as in many organic molecules, it will readily condense into a liquid. The boiling point and the critical temperature will be correspondingly high. Readily condensable vapors are much more soluble than would be predicted from the simple Raoult law.

In close approximation, for a given film material there exists a linear relationship between the logarithm of the solubility and the boiling point of the dissolved gas:

$$\log S = -a + bT_K . \qquad (13)$$

Here S is the solubility; T_K is the boiling point, in $^\circ K$. Thus, the solubility increases, for instance, in the order $N_2 - O_2 - CO_2$.

When comparing the permeability of different types of film material to a given penetrant, a second factor will be found to play a role here, namely the interaction between penetrant and polymer. This can be summarized in the /15 general rule "like dissolve like", meaning that homogeneous molecules readily intermix.

The criteria for determining whether or not this homogeneity exists, are physical-chemical characteristics such as hydrophilic, hydrophobic, polar, apolar.

The size of a molecule (molar volume) is important for diffusion.

This becomes immediately clear if, once again, we consider the diffusion process.

The (amorphous) polymer can be pictured as a tangle of polymer chains and "holes" of molecular size, which continuously disappear and re-form as a result of the thermal agitation of the members of the polymer chains. Diffusion takes place by the displacement of the diffusing molecules from "hole" to "hole" under the influence of a concentration gradient. Small penetrant molecules pass easily through the "holes", which are of the order of magnitude of the molecule diameter and thus have a higher diffusion coefficient. [In this connection for instance, the diffusion constant decreases in the sequence

$$O_2\ (2.98\ \text{Å}) - N_2\ (3.18\ \text{Å}) - CO_2\ (3.32\ \text{Å})].$$

The activation energy for diffusion E_d is the energy required to form sufficiently large "holes" between the molecule segments against the cohesion forces of the polymer to make passage of a penetrant molecule possible. Since larger "holes" are required for larger molecules, E_d will also be greater. For a given polymer, E_d is approximately proportional to the diameter of the molecule of the penetrant.

Molecules in a homologous series of lower molecular weight permeate more rapidly. Molecules of a smaller diameter, of equal molecular weight and equal /16 chemical nature permeate faster.

There exists a clear effect of the molecule shape of the penetrant on the diffusion rate. Linear molecules have a higher diffusion constant than branched molecules which are isomeric therewith.

Shape and size factor may be predominant for substances with little difference in chemical nature (solubility), while they are much less important for molecules with great differences in chemical nature. For example, olefins permeate faster than alkanes of the same structure. The gas permeability for instance always increases in the order $N_2 - O_2 - CO_2$, which indicates that the chemical nature of the diffusing molecules is of greater importance than their geometry. Furthermore, the permeability to water vapor is always much higher than the permeability to N_2, O_2, etc. both as a result of the chemical nature and the dimensions of the molecule (approximately 1/2 O_2 molecule); for polyethylene, the ratio is $P_{H_2O} : P_{O_2} = 225$).

3.4 Nature and Molecular Structure of the Polymer Film

In predicting the factors that influence the permeability (and thus also the solubility and diffusion coefficient), it can be stated quite generally that anything that leads to a decrease of the bonds between the chains or the packing density of the polymer will cause the permeability to increase. The permeability is always a function of the size and mobility of the separate chain segments which are continually subject to thermal agitation.

The intermolecular bonds in the polymer and the general mobility of the

chain are important since they determine the ease of "hole" formation due to thermal agitation.

The molecular weight of the film material is a factor of little influence /17 on the permeability. Neither the solubility nor the diffusion coefficient generally are changed by it.

The "hole" formation is not produced by the swaying motion of the entire polymer molecule entangled with other polymer molecules, but by that of individual chain segments; in this connection the length of the entire molecule is immaterial. Its influence is only noticeable in so far as it manifests itself over other factors, such as crystallinity and density of the amorphous regions.

It has been noted already that the interaction between penetrant and polymer is an important factor for the solubility.

The nature of the polymer (polar, apolar, hydrophilic, hydrophobic) has an influence on the solubility of the penetrant.

As known, there is a general tendency for homogeneous molecules (chemically or electrically homogeneous) to associate and to dissolve into each other, to a much greater extent than is the case for heterogeneous molecules.

A penetrant molecule that is homogeneous with the polymer molecule is more readily absorbed; it then weakens the intermolecular bonds of the polymer with the result of easier formation of "holes" and thus of higher permeation velocity.

The homogeneity may be structural or may be one of approximately equal dipoles in the polymer and penetrant. Thus polyethylene, with a dipole moment (approximately) of zero is closer in nature to benzene and carbon tetrachloride than, for instance, propyl alcohol.

Other combinations of homogeneous molecules, at least in so far as dipole /18 moments are concerned, include - for example - polyvinyl alcohol and water, and cellulose acetate - ethyl acetate.

If the active site on which the diffusing molecule is adsorbed had previously been in interaction with another part of its chain or with an adjoining chain, thus forming an intra- or intermolecular bond, then the adsorption of a penetrant molecule may weaken or even completely rupture this bond. This increases the probability of "hole" formation as a result of thermal agitation and, furthermore, may enlarge the surface of active sites available for adsorption of diffusing molecules.

The capability of a polar polymer to induce a dipole in the diffusing molecule must also be taken into consideration. On this basis it is possible to explain the anomalously high permeability of cellulose acetate and vinylidene chloride/acrylonitrile polymers to benzene, as compared to their low permeability to hexane and carbon tetrachloride; benzene is known to have a high polarizability.

Thus, the solubility of nonpolar gas molecules is, in general, greater in

films with nonpolar molecules than in films with polar molecules. On the other hand, the solution of polar gas molecules is strongest in films having polar molecules.

The solubility of gases in plastics, however, is only slight (generally, < 0.2 vol.% at 1 atm) and, therefore, plays a subordinate role in the permeation. Because of this low solubility, several gases simultaneously dissolved in a polymer, do not affect their individual solubility and (consequently) also not their diffusion coefficients (Ref.5).

A comparison of the gas and vapor permeability shows the great importance of the interaction between polymer and diffusing molecule for the permeability. The permeability constant is 1000 - 100,000 times greater for vapors (e.g., benzene and ethanol) than for gases (CO_2, H_2S), for example, the systems /19

benzene / CO_2 | polyethylene and | C_2H_5OH / H_2S | cellulose.

Since the vapor molecules are at least as large as the gas molecules, the gas permeability must be a reasonable measure of the maximum number of "holes" available for either vapor or gas transmission.

Therefore, almost the entire vapor permeability must be ascribed to the interaction between vapor and polymer.

This interaction includes the rupturing of intermolecular bonds in the polymer and vapor solution.

The diffusion process is strongly influenced by the structure of the polymer. The temperature-independent portion of the diffusion constant is linked with the number of "holes" or the "looseness" of the polymer structure.

A "loose" structure, for instance, because of the asymmetry of the molecule, produces a high rate of diffusion.

Comparing, for example, polyethylene with natural rubber which has similar cohesion energies, it will be found that the diffusion constant for rubber is much greater in connection with the substantially "looser" structure, as a result of the lack of symmetry of the molecules.

If the symmetry is such that intensive crystallization is possible, even if the inter-chain bonds of the amorphous macromolecules are short (polyethylene), the permeability will be slight.

A comparison of two symmetric polymers of approximately the same structure such as polyvinylidene chloride (Saran) with polyethylene shows that, because of the polarity of the Saran molecule, the diffusion constant is much lower here. Because of the high cohesion energy in polar polymers, less holes are formed. /20

It is clear that extensive groups on the main chains of polymer molecules prevent a close mutual approach of the main chains, by which a compact structure would be formed.

In addition, these groups may occasionally replace or mask the polar groups located on or in the main chains, which reduces the mutual binding forces between the chains. As a result, the formation of "holes" can take place more readily in polymers possessing large and nonpolar side chains. The long butyral side chains of the vinyl butyral/vinyl alcohol copolymer for instance in general appear to strongly enhance the permeability, except to water vapor. The OH-groups of polyvinyl alcohol, which result in strong intermolecular bonds and which have a strong attraction for water, are here partially replaced by the large less hydrophilic butyral groups.

It is probable that the diffusion of water is increased as a result of "hole" formation, but the solubility must be strongly reduced, with a great decrease in the rate of permeation as the final result.

The acetyl side chains of cellulose acetate and the phenyl groups of polystyrene in general cause an increase in permeability for cellulose and polyethylene respectively. By esterification of cellulose, the permeability to water is decreased.

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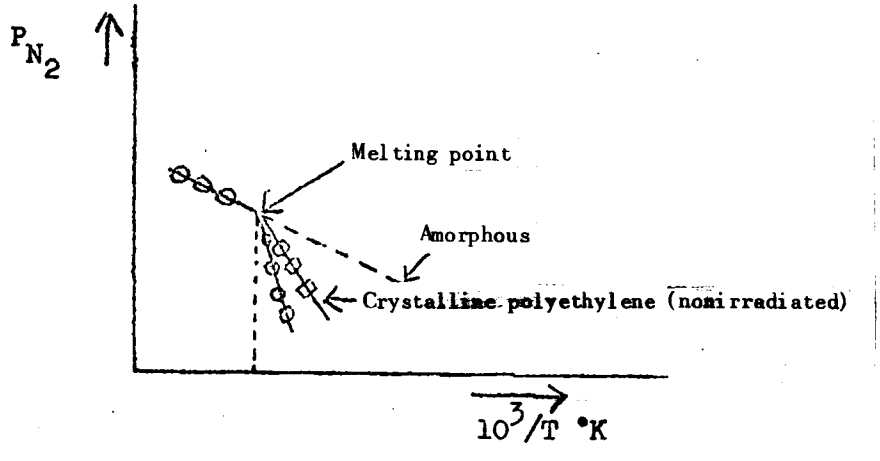


Fig.13 Temperature Dependence of Irradiated and Nonirradiated Polyethylene above and below the Melting Point.
○ irradiated polyethylene
□ nonirradiated polyethylene.

An increasing "bridge formation" between the polymer molecules causes the permeability to decrease strongly. The solubility remains relatively unaffected (even not at all or very slightly affected at extensive bridge formation).

Conversely, the diffusion constant is reduced, since the mobility of the molecule segments decreases, impeding the formation of "holes".

"Crosslinking" may occur, for instance, in polyethylene by irradiation with x-rays. Furthermore, the "crosslinking" makes it possible to heat the polymer above its melting point without losing its shape (Ref.12).

The permeation takes place mainly through the amorphous portion of the

polymer. The crystalline regions are largely impenetrable compared with the amorphous regions of the polymer because of their high cohesion energy (ordered state). Consequently, the solubility as well as the diffusion constant increase with increasing crystallinity of the films. /22

Examples of crystalline polymers, used in the packaging industry, include: polyethylene, polypropylene, polyvinylidene chloride (Saran), rubber hydrochloride (Pliofilm), polymonochlorotrifluoroethylene (Kel-F, Aclar), polyester and polyvinyl fluoride.

Thus, an increase in the crystallinity of plastics leads to lower permeability coefficients.

Orientation, obtained, for instance, by stretching (ordered state) also results in a decrease in gas permeability, since the diffusion coefficient and solubility are lowered (i.a., because of the fact that orientation is accompanied by an increase in crystallinity).

The diffusion coefficient also may be lowered by aging of the film, implying an increase in crosslinking or crystallinity (rubber, regenerated cellulose). The solubility is hardly affected by this.

Thermal and mechanical pretreatment (rate of cooling, tempering, cold-working, hot-working) may set up internal strains (residual stresses), which may have no effect on the solubility but will influence the diffusion coefficient and thus the permeability.

Active fillers reduce the mobility of the amorphous chain segments and in this manner cause the permeability to decrease (reinforcement of silicone-rubber with glass fibers and of natural rubber with mica or carbon black).

To obtain a soft plastic (reduction of glass temperature) plasticizers are used. These must be soluble in the plastic; the agent penetrates between the polymer molecules and thus increases their interstitial distance. /23

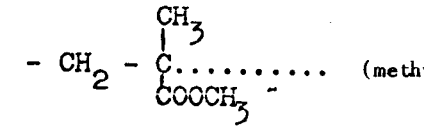
There is no need to add foreign plasticizers. So-called internal softening can also be obtained by introducing bulky groups into the polymer, thus producing a spacing effect, with the same result. By incorporating space-consuming groups into the principal chain of the polymer molecule, steric hindrance can be produced. In this manner, a chain which, in its original state, had many vibration possibilities will become rigid and difficult to move, so that a hard plastic is created.

For instance, polymethylacrylate at room temperature is rubberlike:

$$-CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{H}{|}}{C}}-$$ (methylacrylate unit).

On replacing the H atom by a CH_3 group, it will be found that, despite the distance-increasing CH_3 group which should rather cause an increase in flexi-

bility, a hard plastic is formed:



(methylmethacrylate unit).

Incorporation of a plasticizer into a polymer film, which increases the spacing of the polymer molecules and thus reduces the mutual attraction, leading to an increased mobility of the chain segments, will generally increase the diffusion constant (reduction in activation energy E_d and increase in D_o).

The solubility of the diffusing molecules also is often increased by /24
solution in plasticizer; however, when a hydrophobic plasticizer is incorporated into a hydrophilic film, the solubility of water vapor can be reduced.

Consequently, the addition of a plasticizer need not always lead to an increase in permeability of the film. A reduction in permeability may occur despite spreading of the chains, because of the fact that the number of holes available for diffusion decreases in connection with blocking by the plasticizer, while the solubility may also decrease.

The permeability constants of benzene for glycerol-plasticized films (polyvinyl alcohol, regenerated cellulose) are somewhat lower than for non-plasticized films. Any increase in diffusion as a result of chain spreading thus is more than compensated by the poor solubility of benzene in glycerol (and a possible blocking effect of the plasticizer).

Conversely, dimethoxyethyl phthalate, which is structurally somewhat related to benzene, strongly increases the permeation rate of benzene through cellulose acetate.

The changes brought about in the permeation rate of benzene by addition of glycerol or dimethoxyethyl phthalate as plasticizers are exactly the opposite for ethanol permeation. Cellulose and polyvinyl alcohol, plasticized with glycerol, are substantially more permeable to ethanol than are non-plasticized films. Dimethoxyethyl phthalate appears to reduce the ethanol permeability of cellulose acetate.

The influence of relative humidity on the permeability of plastic films may be considerable. It has been found that water vapor diffuses very rapidly in polymer films. This has little effect for the case of hydrophobic polymers which absorb only small amounts of water vapor.

The situation is different for hydrophilic polymers, such as nylon or cellulose, where the absorbed water acts as plasticizer. This adds itself to /25
the polar centers of the polymer chains by H-bridge formation, as a result of which the relative attraction of the polymer molecules is reduced and the mobility of the chain increased.

The diffusion constant increases strongly as a result of the plasticizing effect of the water, giving rise to an increased permeability of the film.

Sorption of water vapor by hydrophilic foils may increase the solubility of the diffusing molecules. Any possible blocking effect of the water is fully compensated by swelling of the polymer structure, which so greatly weakens the intermolecular forces that the number of existing and potential holes available for gas transmission is increased.

Although in general the absorption of water strongly increases the gas permeability, there are exceptions if the hydrophilic foil does not swell as a result of the absorption of water and if the permeating gas is relatively poorly soluble in water; in that case, the diffusion constant decreases somewhat. For example, the vinyl butyral/vinyl alcohol copolymer (89/11 molar ratio), when saturated with water, is slightly less permeable to CO_2 but more permeable to H_2S than in the dry state. It might be that the blocking effect in the case of CO_2 is stronger than the moderate attraction of H_2O for CO_2 while, in the case of H_2S, the greater solubility in water is predominant.

When the films are prepared from solutions, the influence of the solvent will always remain noticeable.

The diffusion coefficient may vary about 1000-fold for a film not containing a solvent and for the same film containing 10% solvent. /26

The permeability to water vapor of polyvinylidene chloride film prepared from a dispersion in water, is higher than that of extruded Saran film (vinylidene chloride/vinyl chloride copolymer; 85/15 weight ratio).

4. Laminates

Laminates are frequently used in industry for modification of the permeability of plastic foils.

If the permeability constant of the one layer of thickness l_1 is denoted by P_1 and the permeability coefficient of the second layer of thickness l_2 by P_2, then it is simple to calculate from the steady flow condition that the following is valid for the permeability coefficient P of the laminate of a thickness l $(= l_1 + l_2)$:

$$\frac{1}{P} = \frac{l_1}{l} \cdot \frac{1}{P_1} + \frac{l_2}{l} \cdot \frac{1}{P_2} \qquad (14)$$

This equation is valid only if the permeability coefficient is independent of pressure (permanent gases). If the permeability coefficient of the first layer increases strongly with the pressure while that of the second layer does not, then the laminate will be more permeable when the first film is located on the high-pressure side than when it is on the low-pressure side.

Thus, a "valve" action is produced; permeation takes place more rapidly in one direction than in the other. An application of this will be given in Appendix II.

Equation (14) also shows that, if one of the component materials is highly permeable (for example, high P_1 and small $\frac{1}{P}$), then P - by approximation - will be equal to $\frac{l}{l_2 P_2}$.

In this case, the permeability is determined exclusively by the component /27 of low permeability.

Various composites of paper/plastic result in a substantial reduction in gas permeability. This strong effect cannot be attributed to a possible change in structure of the plastic before and after laminating or to a low gas permeability of the paper (which may be full of pinholes), but must be due to a considerable reduction of the effective surface of the plastic by the paper.

Since the permeability is proportional to the surface, it is reduced in proportion to the reduction in surface. Plastic-aluminum composites are among the most gastight films available at present. The aluminum here has the same effect as the paper.

In the packaging industry, mostly Al films of 0.009 - 0.012 mm thickness are used. In general, aluminum foil thinner than 0.03 mm is not free of pinholes.

APPENDIX I

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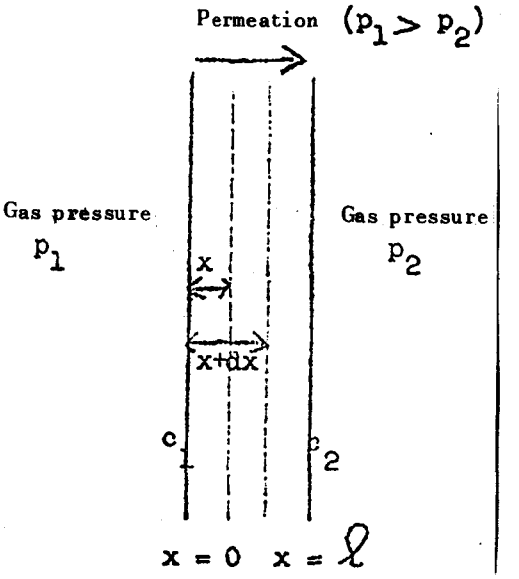
FICK'S LAWS

Let us assume that the sorption and desorption equilibria are rapidly established at the boundary surfaces of the film, so that the diffusion alone is time-determining. The gas permeability has been found to be inversely proportional to the thickness of the film, which points to the fact that the rates of solution and evaporation of the penetrant at the edges of the membrane are high as compared to the rate of diffusion within the membrane.

The combination of the gas in the membrane along the interface thus is constant in practice and independent of the diffusion rate.



Let us now consider the case of diffusion through a film of unit surface with a thickness ℓ, bounded by two parallel surfaces, $x = 0$ and $x = \ell$, which are kept at constant concentrations, c_1 and c_2 respectively $(c_1 > c_2)$ (see accompanying diagram).

In practice, in the case of such a diffusion in a plane plate, it can be assumed that practically all substances diffusing through the surface pass through the edges in a negligible amount, limited by the one-dimensional diffusion equation of Fick. /30

Fick noticed that the diffusion process, i.e., the transport of matter from one portion of the system to another, as a result of random molecular motion, shows a distinct analogy with the transport of heat by conduction which also is the result of random molecular motion. Consequently, for a quantitative description of diffusion, he made use of the mathematical equation for heat conduction

derived several years earlier by Fourier.

1. Fick's First Law

Fick's First Law of (linear) diffusion (1855) which by origin is empirical in character, states the following: The amount of substance diffusing in unit time through a given plane x of unit surface, is proportional to the concentration gradient between the plane x and the plane x + dx infinitely close to it, measured perpendicular to the plane x. Thus,

$$J = -D\frac{\delta c}{\delta x} \qquad \left(\text{Fick's First Law}\right). \tag{2}$$

Here, J is the diffusion rate per unit surface; c is the concentration of the diffusing substance; x is the space coordinate measured perpendicular to the plane of reference; D is the diffusion coefficient [= specific diffusion rate which is a measure for the amount of substance that should be diffused per unit time through unit surface by unit concentration gradient (assuming that the velocity is constant during that time)]. The negative sign appears in the equation, since the diffusion takes place in a direction opposite to that of increasing concentration. (Vector notation: $\vec{J} = -D \text{ grad } c$; the vector J of the diffusion current is in opposite direction to the concentration gradient c; the plane of reference must be taken perpendicular to the direction of this vector.)

(The mathematical equation, taken strictly, is valid only for an isotropic medium whose structure and diffusion properties, in the neighborhood of any point, are relatively the same in all directions. /31

Because of this symmetry, the diffusion current at any point along the normal to the surface, is then of constant concentration through that point.)

Fick's First Law gives the rate of permeation in the steady state through unit surface of the medium, for a given constant concentration gradient over the thickness of the medium and a constant coefficient D.

2. Fick's Second Law

Fick's Second Law relates to the accumulation of matter at a given point in a medium as function of time, and thus refers to the nonsteady state of flow. The Second Law can be derived from the First by considering diffusion in the +x direction.

When there is diffusion only in the +x direction and the increase in substance is considered within an element of volume bounded by two parallel planes, perpendicular to the x direction of unit surface located at x and x + dx (see preceding diagram), then the rate of accumulation will be

$$J_x - J_{x+dx} = D\left[\left(\frac{\delta c}{\delta x}\right)_{x+dx} - \left(\frac{\delta c}{\delta x}\right)_x\right] =$$

$$D\left[\frac{\delta}{\delta x}\left(c + \left(\frac{\delta c}{\delta x}\right)dx\right) - \left(\frac{\delta c}{\delta x}\right)_x\right] = D\frac{\delta^2 c}{\delta x^2}\,dx.$$

On dividing by the volume dx 1 cm of the element, the following expression is obtained for the increase in concentration with time for the limit $dx \to 0$:

$$\frac{\delta c}{\delta t} = D\frac{\delta^2 c}{\delta x^2} \qquad \text{(Fick's Second Law)} \qquad (3)$$

for one-dimensional (or linear) diffusion, derived on the assumption that D = const.

APPENDIX II

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APPLICATION OF LAMINATES

For strongly hydrophilic films, for example cellophane, the gas permeability is largely dependent on the humidity of the film. In the high-vacuum method, 0% relative humidity is obtained at the underside of the film. To determine the gas permeability of cellophane at 100% relative humidity, the hydrophilic film can be conditioned to this humidity by using a "sieve-film" of high gas permeability and low water vapor permeability, such as polyethylene.

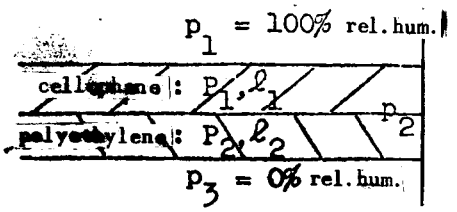
The relative humidity in the boundary layers can be calculated in a simple manner; for a combination of two (or more) films, it always holds that, for the steady state, the diffusion current density J is constant for each layer. Thus,

$$J = P_1\frac{p_1 - p_2}{l_1} = P_2\frac{p_2 - p_3}{l_2} \left(= P\frac{p_1 - p_3}{l}\right)$$

where p_1, p_2, and p_3 are the pressures on either side of the layers; P_1 and P_2 are the permeability coefficients; l_1 and l_2 are the thicknesses of the layers.

Let us assume a relative humidity of 100% at the upper side of the laminate and of 0% at the underside. Then,

$$J = P_1\frac{100\%\ (\text{rel.hum.}) - p_2}{l_1} \longrightarrow 100\% - p_2 = \frac{l_1}{P_1}J$$



$$J = P_2 \frac{p_2 - 0\%\,(\text{rel. hum.})}{\ell_2} \longrightarrow p_2 - 0\% = \frac{\ell_2}{P_2} J$$

From these two relations, on eliminating J, we obtain

$$\frac{100\% - p_2}{p_2} = \frac{\ell_1}{P_1} \times \frac{P_2}{\ell_2} \longrightarrow 100\% - p_2 = \frac{\ell_1}{\ell_2} \cdot \frac{P_2}{P_1} p_2$$

$$\left(1 + \frac{\ell_1}{\ell_2} \cdot \frac{P_2}{P_1}\right) p_2 = 100\%\,(\text{rel. hum.})$$

$$p_2 = 100\%\,(\text{rel. hum.}) \left(\frac{\ell_2 P_1}{\ell_2 P_1 + \ell_1 P_2}\right). \qquad (15)$$

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A film can be conditioned to a certain relative humidity by varying the thickness of the sieve-film and the relative humidity at the upper side of the laminate. If $t_1 = t_2$, it follows from eq.(15) that

$$p_2 = 100\% \frac{P_1}{P_1 + P_2} = 100\%\,\text{rel. hum.} \frac{P_2}{\frac{1}{P_1} + \frac{1}{P_2}}.$$

Since $p_1 \gg p_2$, we have by approximation $p_2 = 100\%$ rel. hum.; thus, the gas permeability of cellophane can be determined, while the film is conditioned to 100% rel. hum.

REFERENCES

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1. Barrer, R.M.: Diffusion in and through Solids. Cambridge, 1951.
2. Jost, W.: Diffusion in Solids, Liquids, Gases. Academic Press, New York, 1952.
3. Crank, J.: The Mathematics of Diffusion. Oxford, 1956.
4. Moll, W.L.H.: Kolloid-Z., Vol.167, No.55, 1959.
5. Rogers, C., Meyer, J.A., Stannett, V., and Szwarc, M.: Tappi, Vol.39, p.737, 1956; Vol.39, p.741, 1956; Vol.40, p.142, 1957.
6. Müller, F.H. and Hellmuth, E.: Kolloid-Z., Vol.144, p.125, 1955.
7. Huldy, H.J.: Plastica, Vol.15, p.146, 1962; Vol.15, p.210, 1962.
8. Korte-Falinski, M.: J. Chim. Phys., Vol.59, No.1, 1962.
9. Bent, H.A.: J. Polymer Sci., Vol.24, p.387, 1957.
10. Binning, R.C., Lee, R.J., Jennings, J.F., and Martin, E.C.: Ind. Eng. Chem.,

Vol.53, No.45, 1961.
11. Stannett, V. and Yasuda, H.: J. Polymer Sci., Part B, Vol.1, p.289, 1963.
12. Rogers, C.E., Myers, A.W., Stannett, V., and Szwarc, M.: Plastics Progr., Vol.45, 1957.

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